

# Heavy Metals Pollution Index in African River Prawn (*Macrobrachium vollenhovenii*) collected from Calabar River, Nigeria.

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**Abstract**—Studies on the accumulation of some heavy metals in African river prawn (*Macrobrachium vollenhovenii*), in Calabar River, Calabar, Cross River State, Nigeria, A total of 54 prawn samples, were collected during the study. The heavy metals in the samples were analyzed using atomic absorption spectrophotometer for cadmium, cobalt, chromium, copper, mercury, manganese, nickel and lead while total hydrocarbon (THC) was analysed using UV-spectrophotometer. The heavy metal concentrations in prawn varied across sampling stations and between seasons. The mean metal concentrations in prawns were:  $0.02 \pm 0.01$  mg/kg (Cd),  $0.45 \pm 0.04$  mg/kg (Co),  $0.06 \pm 0.04$  mg/kg (Cr),  $0.56 \pm 0.04$  mg/kg (Cu),  $0.63 \pm 0.03$  mg/kg (Mn),  $0.67 \pm 0.03$  mg/kg (Ni),  $0.08 \pm 0.01$  mg/kg (Pb) and  $0.69 \pm 0.19$  mg/kg (THC). Mercury was not detected in the prawns. The prawns from Calabar River have high chromium, nickel and THC concentrations according to WHO standard and as such consumption of the prawns is not safe. There should be increase awareness on the impact of unlawful dumping of wastes in the study areas. More studies in the Calabar River aimed at monitoring of pollution should be carried out and properly funded to give an insight into whether the fishery resources in the study area are safe for consumption or not

**Keywords**—Heavy metals, Prawn, Bioaccumulation, Pollution, Bioindicators.

## I. INTRODUCTION

Pollution is the direct or indirect production or introduction by man of energy sources or substances into the atmosphere, terrestrial or aquatic environment resulting in deleterious effects which could jeopardize human health, harm other living resources in the environment and damage or impede the use of amenities or other legal use of the environment [1]. Environmental issues in Nigeria did not gain relative importance until the case of 1988 Koko toxic waste dumping which brought awareness on the need to create the Nigerian Federal Environmental Protection Agency (FEPA) by the Federal Ministry of Environment and other appropriate agencies to handle environmental issues in the country. In Nigeria, pollution of the aquatic environment has continued to generate *unpleasant* health and economic implications in the development of the country [2].

To expose the existence of pollutants and also to evaluate their lethal effects, the use of biological indicators becomes necessary [3]. Biological indicators are species of

living organisms used to examine the state of the ecosystem or the environment [4]. They show the presence of a pollutant by the presence of a characteristic symptom or quantifiable response. They also include biological processes or communities that are used to assess the quality of the environment and how these changes happen with time [5]. An example of this group includes the shrimps, copepods and prawns that are present in the aquatic environments. Such organisms are examined for any change i.e. (physiological, behavioural or biochemical) that may be a sign of trouble within the ecosystem. They give us information about the cumulative effects of various pollutants present in the ecosystem and the duration a problem might have persisted, which chemical and physical testing alone will not do [6]. The relevance and importance of bioindicators compared to man-made equipment are emphasized by [7], who stated that “There is no better indicator of the status of species or a system than the species or system itself or both.”

Prawns refer to some decapod crustaceans. They are abundant and are mostly found feeding at the water bottom

in estuaries, rivers and lakes. They are well-known for feeding on a range of various small epibenthic animals mostly crustaceans, polychaete and other molluscs, this was a result of a study in which various food items were found in the gut of *Macrobrachium vollenhovenii*, they include chlorophytes, copepods, protozoa and diatoms [8; 9]. Planktons such as copepods are used as indicators of pollution [12]. Larger prawns are prone to be targets of commercial exploitation [10]. Prawns are an excellent source of protein. They are high in protein, calcium and iodine but low in carbohydrate. As a result of the rich source of protein in prawns, they are being consumed in so many different culinary traditions [11]. Prawns are eaten by local fishermen and people from all walks of life as fresh, boiled or smoked and this is as a result of its perceived and known documentaries on its nutritional benefits and their accessibility [11]. Decapod crustaceans such as prawns have been handy and are regularly used in heavy metal pollution monitoring [12].

Several studies have encouraged the continuous monitoring of the Calabar River [13] reported a slightly affected river and therefore encouraged continuous monitoring of the Bonny/New Calabar River estuary. [14] reported results that showed that the heavy metal contents in the soil samples from Calabar Ports Authority studied are within WHO limits but also encouraged regular monitoring by relevant authorities. [15] also reported parameters measured as within the permissible limits of WHO and FEPA, but also encouraged sustenance of the ecological status of the Calabar River through waste management practice.

Industrial activities like dredging, fishing and indiscriminate discharge of solid and liquid waste including ballast water, elicit chemicals and contaminants into the environment which causes harm to the aquatic and terrestrial environment and their livestock. As a result of these activities around the study areas, it is suspected that some pollutants might have been introduced into these water bodies which can affect the aquatic lives in them. It is, therefore, necessary to evaluate and know the extent of the damage that might have been done in these aquatic lives, this will provide scientific information for agencies that are responsible for the environment and also provide strategies on how to curb pollution within the study area and create public awareness for the safety and protection of man.

### 1.1 Heavy Metal Pollution

Heavy metals are elements that have a high density and they are harmful in low concentrations [16]. They are naturally part of the earth's crust. These elements can

neither be degraded nor destroyed. They are well-known as insidious lethal pollutants and their presence in the aquatic environment is of great concern since they bio accumulate in aquatic organisms [17]. Metal reservoirs in the aquatic environments include the biota, water and sediment. They tend to bio accumulate in the aquatic organisms. Mercury and lead have no known use in the body while chromium, zinc, copper, manganese and iron are required in the body in minute quantities.

Mercury is a well-known toxic element that has no known function. Natural biological occurrences may cause the formation of methylated derivatives of mercury which bio accumulate in living organisms. Mon methyl mercury and dimethyl mercury, which are the two forms of methylated mercury are highly toxic, they cause neurotoxic logical disorders. The food chain is the major pathway for mercury contamination [16].

The toxicological characteristics of cadmium are derived from the similarity of the element to zinc in chemical properties, which is an essential micro-nutrient in plants, animals and man [16]. It can be bio-persistent. Once it is absorbed by a living organism, it remains in its system for several years (for humans, this may be in decades), though it is excreted eventually.

Copper is widely used by man in the industries and for agricultural purposes. It can be released into the environment by either nature or anthropogenic activities. Examples of natural sources that release copper into the environment include decaying vegetation, forest fires and wind-blown dust [18]. It is an essential micronutrient; in high concentration, it causes kidney and liver damage, anaemia, irritations of the stomach and intestine. People suffering from Wilson's disease stand a higher risk from health effects caused by over-exposure to copper [16]. It normally occurs in chemicals used to control algal growth and in drinking water pipes made from copper [18].

Bioaccumulation is the process by which toxic substances accumulate in the tissues of living organisms over some time. Some heavy metals commonly studied include nickel (Ni), lead (Pb), mercury (Hg), copper (Cu) and cadmium (Cd). They enter our bodies through contaminated water and food. Some heavy metals are needed to maintain the body metabolism, they are referred to as essential heavy metals, they include copper (Cu) and zinc (Zn).

Copper, lead, and manganese is heavy metals that get into the aquatic environment through run-offs from farmlands where agrochemicals have been used, these agrochemicals contain heavy metals such as cadmium, manganese and lead [19]. Some human sources of pollution

include metal processing, industrial effluents, fertilizers, solid waste disposal, fossil fuels, mining and coal combustion. Some natural sources of pollution include windblown dirt and weathering of rocks [20]. Some industries that produce batteries and paints, ceramics, steel, cement and petroleum refining are being located haphazardly especially near populated and residential areas [20]. The industrial effluents from factories are often disposed of untreated into open drains, streams and rivers. It has caused a rise in the levels of some heavy metals found in the aquatic ecosystem.

Some of the sources of cadmium in the aquatic ecosystem include leakage from Ni-Cd batteries (nickel-cadmium batteries) and run-off from farmlands where fertilizers containing phosphates are being applied [21]

Advancements in the use of technology and increase in the population have led to environmental concerns as a result of the haphazard dumping of waste, disposal of industrial effluents and wastes from petroleum in water and spilt crude oil in the environment [22].

### 1.2 Effect of Heavy Metal Pollution

Essential metals can also be potentially harmful to aquatic lives when they build up above limits. They have been reports on their harmful ecological impacts as pollutants can accumulate in the aquatic food chain causing great risk for a man [23] and aquatic habitat. Exposures to high lead level causes biochemical toxic effects in man. This, in turn, results in problems in the production of haemoglobin, kidney, gastrointestinal tract, acute and chronic damage to the nervous system [16]. Lead is an environmental pollutant known to cause damage to man, affecting especially the central nervous system, reproductive organs, kidney and the immune system [24]. There is the absorption of about 50% of inhaled organic lead in the lungs and adults take up to 10 – 15% of the metal in contaminated foods [24]. Behavioural disturbances, difficulties in learning and concentration are some of the symptoms that can also be seen in children [25].

Chromium accumulates in aquatic lives; this adds to the risk of consuming fish that has been exposed to high concentrations of chromium [16]. The effect of mercury poisoning is primarily in the central nervous system. Exposures to mercury are extremely toxic to the brain, kidney and developing foetus [26]. In man, lead exposure can lead to various biological effects based on the exposure level and duration [16]. Accumulation of heavy metals occurs via the food chain and it is finally assimilated by man which results in complications in health [27]. According to [28], non-essential heavy metals such as

mercury (Hg), lead (Pb) and cadmium (Cd) have attracted global attention as a result of their great toxic effects on the aquatic biota. Essential metals can also be potentially harmful to aquatic lives when they build up above limits.

The accumulation of these metals in the biota was reported to be dependent on the chemical effects of the metal on the lipid content constituents of biological tissue and its propensity to bind to a particular material [28].

## II. MATERIALS AND METHODS

### 2.1 Description of Study area

The location of the area of study is at Calabar River Latitude N4° 57' 326"; Latitude E8° 18' 557". The area of study has a climate that is well known to have a long-wet season from April to October and a dry season between November to March [30]. The total annual rainfall is about 2000 mm. There is always a brief interval of drought in the wet season usually by August and September, this is called August drought. There is also a usual cold, dry and dusty period between December and January usually known as harmattan season [31]. The river has its downstream or lower reaches influenced by semi-diurnal ocean tides [30]. It has a high level of biodiversity which supports a wide variety of aquatic organisms which are all rich sources of protein to the coastal and upland dwellers [32].

Calabar River has been described as forming a part of the tidal tributaries of the Cross-River estuary in Nigeria[30]. The river is known to drain through the heavy rain forest formations and landscape in the southern part of Nigeria [33]. Calabar River has mangrove vegetations namely *Rhizophora racemosa*, *Avicennia africana* and *Nypafruticans*. The vegetation also contains palm trees (*Elias guineensis*) as well as African oak species (*Oldfieldia africana*) [34].

#### 2.1.1 Stations of the study area

This research was carried out at different points in Calabar River namely: Adiabo beach (station 1), Nigerian Ports Authority (NPA) (station 2) and Nsidung beach (station 3).

*Station one:* is located at Latitude 5° 3' 27.23" N and Longitude 8° 18' 23.53" E along Calabar River. This station is at Adiabo beach. It is taken as the control station. Sand mining and fishing are the activities common in this station. The vegetation surrounding this station includes Nipa palm (*Nypafruticans*), palm trees (*Elias guineensis*) and Africa oak species (*Oldfieldiaafricana*).

*Station two:* is located at Latitude 5° 044' 19" N and Longitude 8° 19' 13" E by the Nigerian Ports Authority,

Calabar. The Mangrove vegetation surrounding this station include Nipa palm (*Nypafruticans*) and palm trees (*Elias guineensis*). It is very common to see Nipa palms around the coastline of several rivers [35] including rivers in Nigeria. This station is a harbour for ships. Emissions from the ships go directly into the water body. [36] reported that ballast water allows for a favourable environment for microorganisms such as viruses, bacteria to move to another location and cause harmful effects on the local flora and fauna through their toxicity and over-competitive abilities. [37] had reported the presence of certain bacteria and viruses that cause human epidemic cholera in ballast water in the coastal marine communities in North America.

**Station three:** This station is located at Latitude 4° 57'26.76" N and Longitude 8°18'40.02" E. It is open and unrestricted from anthropogenic activities. A large market is located at the bank of this station and indiscriminate disposal of solid and liquid wastes goes on here. Nipa palm (*Nypafruticans*), palm trees (*Elias guineensis*) and oak trees (*Oldfieldiaafricana*) are predominantly seen around the coastlines of this river.

## 2.2 Sample Collection

The prawn samples were collected at the three different stations, from August to January. Prawn samples were collected with the help of local fishermen who were pre-informed a day before the sampling day. Immediately after collection, they were preserved in an icebox containing ice blocks to prevent deterioration. After the collection of these prawn samples, they were transferred to the Chemistry Department of the University of Calabar, Cross River State for atomic absorption spectrophotometer analysis of heavy metals. The metals analysed were copper (Cu), mercury (Hg), chromium (Cr), cobalt (Co), cadmium (Cd), manganese (Mn), lead (Pb), nickel (Ni) and total hydrocarbon (THC).

## 2.3 Heavy Metal Analysis

The prawn samples were analysed for the presence of heavy metals. They were washed with deionised water, put in a clean plastic bag, stored and frozen until analysis was carried out. The prawn samples were oven-dried at 109 °C and ground. One gram of the prepared and ground prawn samples was weighed using a weighing balance (model: BG ADAM ®) into a 250 ml beaker. Five millilitres of perchloric acid and 10 ml of nitric acid were added into the beaker. The mixture was heated until the whole sample digested to a clear solution. The solution was allowed to cool off before it was decanted into a plastic sample bottle and stored until the concentration of heavy metals in it was determined with AAS (Atomic Absorption

Spectrophotometer) [38]. Heavy metal levels were expressed in mg/kg.

## 2.4 Statistical Analysis

All metal concentration values were subjected to descriptive statistics (Mean, standard error and ranges). T-test was used to find out any significant difference in the concentration of heavy metals in prawns. All statistical analysis was carried using version 20 of SPSS at 0.05 level of significance.

# III. RESULTS AND DISCUSSION

Table 1: Heavy Metals concentration in Prawns

Metal (mg/kg)	Location			WHO, 1999
	Station 1 Adiabo	Station 2 N. P. A	Station 3 Nsidung Beach	
<b>Cd</b>	0.03± 0.02	0.03±0.01	N. D	<0.01
<b>Co</b>	0.47±0.03	0.30±0.08	0.59±0.05	-
<b>Cr</b>	0.19±0.12	N. D	N. D	<0.01
<b>Cu</b>	0.72±0.09	0.42±0.02	0.53±0.03	0.1
<b>Hg</b>	N. D	N. D	N. D	-
<b>Mn</b>	0.64±0.02	0.56±0.04	0.68±0.07	5.0
<b>Ni</b>	0.63±0.04	0.77±0.06	0.59±0.01	0.02
<b>Pb</b>	N. D	0.12±0.01	0.12±0.01	0.05
<b>THC</b>	0.59±0.28	0.48±0.37	0.99±0.49	0.01

Keynote: ND = Not detected Mean ± Standard Error

## 3.1 Heavy metals in Prawns

The heavy metal concentrations in the prawns sampled from the three study locations are shown in Table 1.

Mercury was not detected in prawns from the 3 sampling stations. The heavy metal concentration in the study area varied across sampling stations. These differences in the mean heavy metal concentrations show varying levels of contamination, they also suggest a build-up of certain heavy metals in the prawn tissues [39].

Cobalt, copper and lead concentration in the prawn samples varied significantly ( $P<0.05$ ) across sampling stations. This implied that the differences in the level of anthropogenic inputs which introduced cobalt, copper and lead were not the same across the 3 sampling stations and so had a significant influence on their distribution.



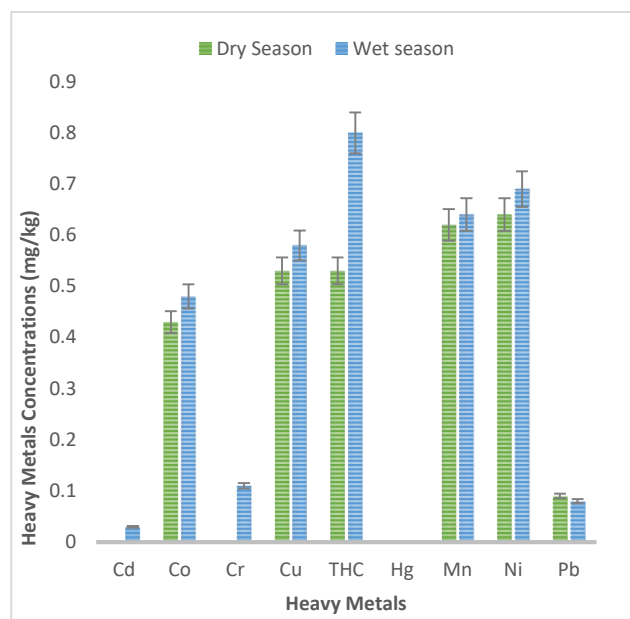


Fig. 1: seasonal variations in the concentrations of heavy metal in prawns from Calabar River.

On the other hand, the levels of concentration of cadmium, chromium, manganese and THC did not vary significantly across the 3 sampling stations at  $P > 0.05$ . This implied that the levels of anthropogenic inputs in the 3 sampling stations were at par with those of cadmium, chromium, manganese and THC levels.

[40] reported lower values of chromium and nickel and higher value of copper in *Macrobrachium vollenhovenii*, whereas, alower value of chromium and nickel and higher levels of copper and lead for *Penaeus notialis*. The discrepancies in the heavy metal levels between the reports and that of the present study could be as a result of the differences in levels of anthropogenic activities, study area, study period, study duration and geographical locations. The differences could be as a result of the variations in the extent to which the bioaccumulation of heavy metals in prawns depends on the effect of the chemicals on the organism, its affinity to bind to a particular material and also on the lipid content and its composition of the prawn tissues between the studies as stated by [29]. These discrepancies could also be due to differences in prawn species and prawn age between the different studies.

Chromium and THC concentrations in prawns from Calabar River were above the WHO acceptable range, nickel was above WHO and FAO permissible limit. This implies that the prawns from the study area have high concentrations of chromium, nickel and THC and as such, they may be unsafe for consumption.

Adiabo (Station 1) recorded the highestcopper concentration ( $0.72 \pm 0.09$  mg/l) followed by Nsidung beach ( $0.53 \pm 0.03$  mg/l) and N.P.A ( $0.42 \pm 0.02$  mg/l), this was similar to the report of [41] who reported the highest copper ( $2.79 \pm 0.02$  mg/l) concentration in Ikom (Station 1) ( $p < 0.05$ ) and minimum concentration of copper ( $1.0 \pm 0.001$  mg/l) in prawn samples from Calabar river.

### 3.2 Seasonal variation in the concentrations of heavy metal in prawns

Figure 1 shows a bar chart of the variations in the heavy metal concentrations in prawn samples (mg/kg) from the Calabar River during the dry and wet season. Seasons usually influence the accumulation of heavy metals in the tissues of a biological organism. In this study, there were variations in the mean concentrations of the heavy metal in the rainy and dry season. These seasonal variations may be as a result of the fluctuations in the number of sewage effluents, run-offs and industrial discharges into the river [42]. The mean cadmium, chromium, cobalt, copper, THC, manganese, nickel and lead levels did not vary significantly between the rainy season and dry season even though most of the metals had higher concentration during the rainy season compared to the dry season. This could be due to the intense discharges of organic pollutants from surface water run-offs and drainage channels into the river during the rainy season thereby leading to high values of these mentioned metals during the rainy season. Similar observations were reported by [43] who reported higher concentrations of copper and chromium in shrimps during the rainy season than during the dry season. In contrast to these, the mean levels of lead in prawns were higher during the dry season than during the wet period. This could be as a result of discharges from industrial and municipal wastes into Calabar River when diluting water was reduced due to lack of rain. These variations in the observation could be due to the differences in the study area, study period, study season, study duration and geographical area.

## IV. CONCLUSION

The levels of heavy metals in prawns, varied among the 3 sampling stations. The cobalt, copper, lead concentrations in prawns varied significantly while the levels of the concentration of cadmium, chromium, manganese and THC did not vary significantly among the sampling stations. Mercury was not detected in the prawns.

The distribution of heavy metals in prawns, water, sediment and Physico-chemical parameters were heavily influenced by seasons. Cadmium, chromium, copper, cobalt, THC, manganese and nickel concentration in prawns were higher during rainy season while lead was

higher during the dry season. Cadmium, chromium, cobalt, copper, THC, manganese, lead and nickel concentration in prawns from the study area varied significantly between the rainy and dry seasons.

The prawns from Calabar river has high chromium, nickel and THC concentrations according to WHO, FEPA and FAO standards and as such are unsafe for consumption, this could lead to various health problems in the community [44]

In conclusion, the study revealed variations in the levels of THC and heavy metals in prawns across the sampling stations. The study also revealed that various human activities in the study area may have influenced the concentrations of heavy metals and THC in prawns.

#### 4.1 Recommendations

The disposal of wastes in the study area may have led to increase in the concentrations of chromium, nickel and THC in prawns, therefore, it is recommended that awareness be created on the impact of indiscriminate disposal of wastes in the study areas. Enforce environmental policy. This can help reduce the indiscriminate disposal of potentially hazardous wastes. More studies should also be funded towards the continuous monitoring of the Calabar River to further reveal underlying pollution.

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